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(54) Title: HAIR CARE COMPOSITIONS CONTAINING POLYSILOXANES

(57) Abstract: A hair care composition which comprises an amino, polyol functional siloxane material, wherein the amino, polyol functional siloxane material may be prepared by reacting certain amino functional siloxane with one or more monoepoxides. Preferred hair care compositions include a shampoo composition, a leave-on conditioner, a semi-permanent colorant or a permanent colorant composition. Hair care compositions according to the invention are found to provide such benefits as improved conditioning, improved feel of the hair, reduction in colour fading and improved wash resistance of colour, depending on the type of composition provided.

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## HAIR CARE COMPOSTIONS CONTAINING POLYSILOXANES

[0001] This invention relates to hair care compositions, and in particular hair-care cosmetic compositions containing certain amino-functional polysiloxanes.

5 [0002] Amino-functional polysiloxanes are known for use in hair care compositions to impart softening and ease of combing. For example, in U.S. Pat. No. 4,563,347 it is disclosed that an aqueous emulsion of aminoalkyl substituted polydimethylsiloxane is useful to condition hair because it facilitates combing and imparts a smooth feel to hair. The aminoalkyl substituents are credited with providing the copolymers with cationic sites that make the polymer more substantive to hair than nonsubstituted polydimethylsiloxane. The patent further teaches the use of aminofunctional polydiorganosiloxane solutions and emulsions as conditioners. Other hair treating compositions containing amino functional polysiloxanes are described in U.S. Pat. Nos. 4,586,518, 4,601,902, and 4,618,689. However, there is always a search for improved performance in such applications. It has now been found surprisingly that certain amino-functional polysiloxanes which also have alcohol functionalities provide such improvements in addition to other benefits when used on hair.

10 [0003] Accordingly, the present invention provides a hair care composition comprising a polysiloxane having both amino and polyol groups. It was surprisingly found that these materials provide benefits in a number of hair care applications, including shampoos, leave-on conditioners and semi-permanent hair colorants. Amino, polyol functionality is defined as a functional substituent where the amine is further substituted with at least one group containing one or more hydroxyl groups.

20 [0004] Suitable amino, polyol functional siloxane materials are known and have been described in the literature. For example EP specification 0399706 describes an amine containing organosilicon compound, for treating textile fibers, which is the reaction product of an organopolysiloxane having at least one unit of the general formula  $O_{3-a/2}SiX_a-R-NH-$   $R'$  and at least one unit of the general formula  $O_{4-b/2}Si-X_b$  with one or more monoepoxides wherein X denotes a monovalent hydrocarbon group having up to 8 carbon atoms, R denotes

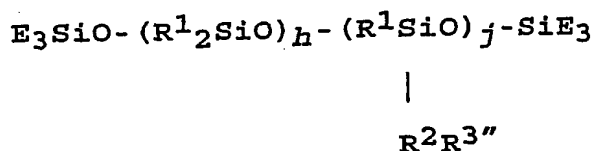
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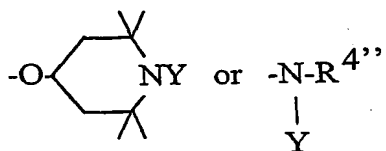
a divalent alkylene group, R' denotes a hydrogen atom or a group of the formula RZ wherein Z is NHX, NH<sub>2</sub>, NHRNH<sub>2</sub> or NHRNHX, a has a value of 1 or 2 and b has a value of 2 or 3.

The epoxides will react with the amine groups.

- 5 [0005] In US patent 6171515 describes as part of a fiber treatment composition which reduces yellowing and adds hydrophilicity to treated textile fibers an amine, polyol functional siloxane having an average general formula



10 wherein each E is independently selected from a monovalent hydrocarbon group, a hydroxyl group or an alkoxy group; each R<sup>1</sup> is independently a monovalent hydrocarbon group; each R<sup>2</sup> is independently a divalent hydrocarbon group having 1 to 10 carbon atoms; h is 25 to 1,000; j is 0.1 to 200; and each R<sup>3''</sup> is a heterocyclic nitrogen-containing group

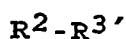
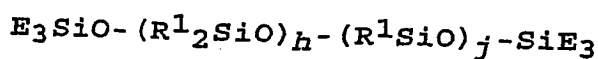


15 wherein each R<sup>4''</sup> is independently selected from a hydrogen atom or a group of formula -R<sup>2</sup>NY<sub>2</sub>, each Y is independently a hydrogen atom or Y', and each Y' is a group of formula -CH<sub>2</sub>(OH)-CHR<sup>2</sup>-OH, wherein R<sup>2</sup>, which can be the same or different, is characterized as above, and with the proviso that every Y is not H;

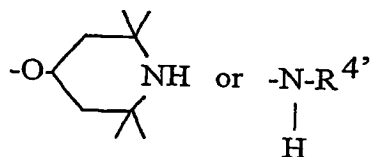
20 [0006] Amine, polyol functional siloxanes used in this invention may be prepared by the following method. First, component (i) an amine functional siloxane is prepared by base equilibration using a catalyst. A preferred method comprises heating to 150°C, a composition comprising a polydiorgano-siloxane; an endblocker, such as hexamethyldisiloxane; an amine functional silane or amine functional siloxane; and water in the presence of the catalyst.

While heating, a mild strip is applied to the system to remove by-products such as water and alcohol. After formation of component (i), the reaction mixture can be further stripped to remove low boiling impurities from component (i). In a particularly preferred embodiment of

the invention, component (i) is formed by a condensation reaction process. The condensation reaction process comprises I) heating a mixture comprising silanol-endblocked polydimethylsiloxane, an alcohol and an aminosilane, in the presence of a catalyst, and thereafter II) gradually reducing pressure to promote condensation polymerisation by removing by-products from the reaction mixture. The alcohol is preferably a blend of linear alcohols having 10 to 15 carbon atoms. Suitable alcohols are commercially available. Component (i) the amine functional siloxane has the average general formula:



where  $R^1$ ,  $R^2$ ,  $h$  and  $j$  are as described above, with  $h$  preferably being from 75 to 400.  $R^{3'}$  is a heterocyclic nitrogen-containing group



where each  $R^{4'}$  is selected from a hydrogen atom or a group of the formula  $-R^2NH_2$ . When component (i) the amine-functional siloxane is prepared by the base equilibration process, each  $E$  is a monovalent hydrocarbon group, preferably an alkyl or aryl group. When the amine-functional siloxane is prepared by the condensation reaction process, each  $E$  is independently selected from monovalent hydrocarbon groups, hydroxyl groups and alkoxy groups. The amine-functional siloxane (i) is then reacted with (ii) an epoxy functional alcohol compound to form component (a) the amine, polyol functional siloxane, described above. Component (ii) is an epoxy functional alcohol compound having a general formula:

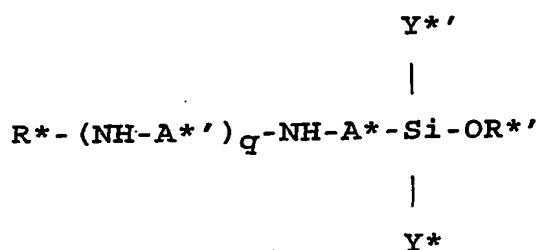


where  $R^2$  is a divalent hydrocarbon group as described above. Suitable epoxy functional compounds for component (ii) include glycidol, 2,3-epoxy-cyclopentanol and 3,3-epoxy-6-methylcyclohexylmethanol. Glycidol is preferred.

[0007] An alternative way of making suitable amino, polyol functional siloxanes is by a process comprising reacting an aminosilane (G) which contains an aminoalkyl group and at least one alkoxy group bonded to Si with a carboxylic acid and a silanol-functional polysiloxane (B\*), whereby the aminosilane (G) is at least partially converted into its carboxylate salt which acts as a catalyst for the condensation reaction between (G) and (B\*).

[0008] The process for making the appropriate amino-functional polysiloxanes is the subject of patent application GB0120058.3 which is incorporated herein by reference. The process described in said patent application is explained briefly below and produces the advantage that the amino-functional polysiloxane reaction product does not contain unwanted catalyst residues. The amine carboxylate salt which acts as catalyst is incorporated in the amino-functional polysiloxane as amine units which are in carboxylate salt form. The amino-functional polysiloxane reaction product does not require filtration, nor does it require heat treatment to decompose the ammonium salt catalyst, which has the risk of generating trialkylamine odour in the product. The amino-functional polysiloxane can be prepared as a clear liquid reaction product.

[0009] The aminosilane (G) contains an aminoalkyl group and at least one alkoxy group bonded to Si. The aminoalkyl group is preferably of the formula  $R^*-(NH-A^{*'})_q-NH-A^*$  wherein  $A^*$  and  $A^{*'}$  are each independently a linear or branched alkylene group having 1 to 6 carbon atoms and optionally containing an ether linkage;  $q = 0-4$ ;  $R^*$  is hydrogen or an alkyl or hydroxyalkyl group having 1 to 4 carbon atoms. Examples of preferred aminoalkyl groups include  $-(CH_2)_3NH_2$ ,  $-(CH_2)_4NH_2$ ,  $-(CH_2)_3NH(CH_2)_2NH_2$ ,  $-CH_2CH(CH_3)CH_2NH(CH_2)_2NH_2$ ,  $-(CH_2)_3NHCH_2CH_2NH(CH_2)_2NH_2$ ,  $-CH_2CH(CH_3)CH_2NH(CH_2)_3NH_2$ ,  $-(CH_2)_3NH(CH_2)_4NH_2$  and  $-(CH_2)_3O(CH_2)_2NH_2$ . The aminosilane (G) preferably has the formula



wherein  $A^*$ ,  $A^{*'}$ ,  $q$  and  $R^*$  are defined as above;  $R^{*'}$  is an alkyl or alkoxyalkyl group having 1 to 6 carbon atoms, for example, methyl, ethyl, butyl or methoxyethyl; and  $Y^*$  and  $Y^{*'}$  are each independently a group  $-OR^{*'}$  or an optionally substituted alkyl or aryl group.

5 [0010] The silanol-functional polysiloxane ( $B^*$ ) is preferably a linear hydroxyl-tipped polydiorganosiloxane. It can for example be a linear hydroxyl-tipped polydimethylsiloxane, preferably a liquid polydimethylsiloxane of degree of polymerisation 4-1000, most preferably 10-100. Alternatively the polysiloxane ( $B^*$ ) can contain 2-30C alkyl, for example, ethyl, propyl, pentyl or hexyl, substituted alkyl, for example fluoroalkyl such as 3,3,3-  
10 trifluoropropyl, or alkenyl, for example vinyl, allyl or hexenyl, groups or aryl, for example phenyl, or aralkyl, for example 2-phenylpropyl, groups bonded to Si. Such groups may for example be present as  $-\text{Si}(\text{CH}_3)\text{R}^{*'}-\text{O}-$  units, where  $R^{*'}$  is 2-30C alkyl or alkenyl, aryl or aralkyl, or as  $-\text{Si}(\text{R}^{*'})_2-\text{O}-$  units. Preferably at least 80% of the total silicon-bonded substituents are methyl groups.

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[0011] The carboxylic acid used in the reaction, which reacts with the aminosilane ( $G$ ) to form a carboxylate salt catalyst, can be chosen from a wide range of carboxylic acids, for example aliphatic carboxylic acid having 1 or 2 up to 20 carbon atoms, preferably at least 4 carbon atoms, which has the advantage of producing a clear liquid reaction product.  
20 Carboxylic acids substituted by an electron-withdrawing moiety, for example halogen such as fluorine or chlorine or a hydroxyl group, may be preferred since amine carboxylate catalysts formed from these acids yield products with considerably reduced odour. Examples of such acids substituted by an electron-withdrawing moiety are lactic acid and fluoroalkanoic acids such as fluoroacetic acid or 4,4,4-trifluorobutanoic acid.

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[0012] The carboxylic acid is preferably used at 0.05-5, particularly 0.1 or 0.2 up to 1.0 or 2.0, % by weight based on the aminosilane ( $G$ ). At this level of addition only a minor proportion of the amino groups of the aminosilane ( $G$ ), for example 0.2-25% of the amino groups, are in carboxylate salt form. Accordingly, only about 0.2-25% of the amino groups in  
30 the amino-functional polysiloxane reaction product are in carboxylate salt form.

[0013] In the process, an alcohol is co-reacted with the aminosilane (G), carboxylic acid and silanol-functional polysiloxane (B\*). The alcohol tends to become incorporated in the amino-functional polysiloxane as an end-blocking alkoxy group. The alcohol can be an aliphatic alcohol having 8 to 30 carbon atoms, for example n-octanol, n-decanol, octadecanol, cetyl alcohol or a commercial mixture of linear and branched 12-16C alcohols. The alcohol can alternatively be an ether alcohol, for example 2-methoxypropanol or 2-butoxyethanol or a hydroxy-terminated polyether, for example a polyethoxylated fatty alcohol or a polypropylene glycol monoether.

[0014] The amino, polyol-functional siloxane can be used in organic solvent solution, a solution in siloxane polymers or in aqueous solution, a dispersion, emulsion or suspension and can be used in free amine form. Compositions containing the amino-functional polysiloxane can contain additional ingredients such as surfactants, thickeners, rheology modifying additives, perfumes, waxes, emollients, cleaning agents, lubricating oils, electrolytes, flavouring agents, biocides, pharmaceutical or cosmetic active materials. Suitable surfactants include non-ionic, cationic or anionic surfactants, and particularly preferred surfactants, if used, are polysiloxane polyoxyalkylene copolymers. These are well known and have been described in a number of publications, e.g. in US patent 6171515, mentioned above, in GB patent specification 2166750 and EP 0381318.

[0015] Copolymers comprising siloxane units and oxyalkylene units are well known and have been commercially employed in applications such as surfactants for example for polyurethane foams and as textile fiber lubricants. In U.K. Patent 1 290 687 there are disclosed siloxane-poly-oxyalkylene block copolymers in which there are present methoxy groups attached to silicon atoms. European Patent Specification 32 310 also discloses copolymers containing siloxane units, oxyalkylene units and silicon-bonded hydrolysable groups.

[0016] In GB 2166750 an organosiloxane-oxyalkylene copolymer is described wherein a silicon atom of at least one organosiloxane unit has attached thereto a group represented by the general formula  $-X^{\#}(OR^{\#})_nOSiR^{\#}_s(OR^{\#})_{3-s}$  wherein  $X^{\#}$  represents a

divalent hydrocarbon group having from 2 to 8 inclusive carbon atoms,  $R^\#$  represents an alkylene group having from 2 to 4 inclusive carbon atoms,  $n$  is an integer of at least 2,  $R^\#$  represents an alkyl group having from 1 to 8 inclusive carbon atoms, a vinyl group, an allyl group or a phenyl group,  $R^\#$  represents an alkyl or an alkoxyalkyl group having less than 7 carbon atoms and  $a$  has a value of 1 or 2, the remaining silicon-bonded substituents in the organosiloxane units being selected from hydrogen atoms, monovalent hydrocarbon groups and groups represented by the general formula  $-X^\#(OR^\#)_nOG^\#$  wherein  $X^\#$  and  $R^\#$  are as hereinabove defined and  $G^\#$  represents a hydrogen atom, a monovalent hydrocarbon group having from 1 to 10 carbon atoms or an acyl group having from 2 to 6 carbon atoms, at least 40 percent of the total substituents bonded to siloxane silicon atoms in the copolymer being methyl.

[0017] In EP 381318 a crosslinked polydiorganosiloxane-polyoxyalkylene copolymer is described, comprising siloxane units (i)  $R_aR'SiO_{3-a'/2}$ , (ii)  $R_bSiO_{4-b/2}$  and at least one bridging unit (iii)  $R_aSiO_{3-a/2}.X.O_{3-a/2}SiR_a$  wherein each R represents a monovalent hydrocarbon group, each R' represents a polyoxyalkylene group linked to the silicon atom through a divalent hydrocarbon linkage, each X represents a divalent organic or organosiloxane group linked to the two silicon atoms of the or each bridging unit (iii) via a Si-C linkage,  $a$  has the value 0, 1 or 2 and  $b$  has the value 0, 1, 2 or 3

[0018] Alternatively a surfactant may be an epoxy, glycol siloxane having the average general formula:  $E_3SiO-(R^1_2SiO)_h-(R^1R^6SiO)_j-(R^1R^7SiO)_k-SiE_3$  wherein each  $R^1$  is independently a monovalent hydrocarbon group,  $R^6$  is an epoxy containing group,  $R^7$  is a polyether group, each E is independently selected a monovalent hydrocarbon group, a hydroxyl group and an alkoxy group,  $h$  is 25 to 1000,  $j$  is 0.1 to 200 and  $k$  is 0.1 to 200. This surfactant may be prepared, for example, by a hydrosilylation reaction of a composition comprising (1) a polyorganohydrogen siloxane, (2) an alkenyl-functional glycol ether, (3) an alkenyl-functional glycidyl ether, (4) a catechol compound and (5) a hydrosilylation reaction catalyst.



[0019] The hair care compositions according to the present invention, comprise the amino, polyol functional siloxanes. It has been found that particularly suitable compositions are shampoo compositions and leave-on conditioners where the siloxanes impart more than usual benefits of conditioning and improved feel to the hair. Additionally it was surprisingly found that the siloxanes provide a benefit in semi-permanent and permanent colorants for hair, where they reduce the colour fading and provide wash resistance of the colour imparted to the hair.

[0020] This invention relates in particular to the use of amino, polyol functional siloxanes to make shampoo compositions. More particularly this invention is directed to a shampoo composition comprising an amino, polyol functional siloxane, and at least one anionic deterative surfactant, with preferably also a foam boosting agent, a pH adjusting agent, a thickening agent, and water. The shampoo composition may be for example optically clear, opaque or pearlescent.

[0021] The anionic deterative surfactant can be any of the well-known anionic deterative surfactants typically used in shampoo formulations. These anionic deterative surfactants function as cleansing agents and foaming agents in the shampoo compositions of this invention. The anionic deterative surfactants are exemplified by alkali metal sulforicinate, sulfonated glyceryl esters of fatty acids such as sulfonated monoglycerides of coconut oil acids, salts of sulfonated monovalent alcohol esters such as sodium oleylisethionate, amides of amino sulfonic acids such as the sodium salt of oleyl methyl tauride, sulfonated products of fatty acids nitriles such as palmitonitrile sulfonate, sulfonated aromatic hydrocarbons such as sodium alpha-naphthalene monosulfonate, condensation products of naphthalene sulfonic acids with formaldehyde, sodium octahydroanthracene sulfonate, alkali metal alkyl sulfates such as sodium lauryl sulfate, ammonium lauryl sulfate or triethanol amine lauryl sulfate, ether sulfates having alkyl groups of 8 or more carbon atoms such as sodium lauryl ether sulfate, ammonium lauryl ether sulfate, sodium alkyl aryl ether sulfates, and ammonium alkyl aryl ether sulfates, alkylarylsulfonates having 1 or more alkyl groups of 8 or more carbon atoms, alkylbenzenesulfonic acid alkali metal salts exemplified by hexylbenzenesulfonic acid sodium salt, octylbenzenesulfonic acid sodium salt, decylbenzenesulfonic acid sodium salt, dodecylbenzenesulfonic acid sodium salt,

cetylbenzenesulfonic acid sodium salt, and myristylbenzenesulfonic acid sodium salt, sulfuric esters of polyoxyethylene alkyl ether including  $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_2\text{SO}_3\text{H}$ ,  $\text{CH}_3(\text{CH}_2)_7\text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_{3.5}\text{SO}_3\text{H}$ ,  $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_8\text{SO}_3\text{H}$ ,  $\text{CH}_3(\text{CH}_2)_{19}\text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_4\text{SO}_3\text{H}$ , and  $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{O}(\text{C}_2\text{H}_4\text{O})_6\text{SO}_3\text{H}$ , sodium salts, potassium salts, and amine salts of alkyl naphthylsulfonic acid.

[0022] Preferably the anionic deterative surfactant is selected from the group consisting of sodium lauryl sulfate, ammonium lauryl sulfate, triethanolamine lauryl sulfate, sodium lauryl ether sulfate, and ammonium lauryl ether sulfate. The anionic deterative surfactant is preferably present in the shampoo compositions of this invention in an amount from about 5 to 50 wt% and more preferably about 5 to 25 wt% based on the total weight of the composition.

[0023] Optionally the shampoo composition also contains a foam boosting agent. The foam boosting agent is preferably selected from the group consisting of fatty acid alkanolamides and amine oxides. The fatty acid alkanolamides are exemplified by isostearic acid diethanolamide, lauric acid diethanolamide, capric acid diethanolamide, coconut fatty acid diethanolamide, linoleic acid diethanolamide, myristic acid diethanolamide, oleic acid diethanolamide, stearic acid diethanolamide, coconut fatty acid monoethanolamide, oleic acid monoisopropanolamide, and lauric acid monoisopropanolamide. The amine oxides are exemplified by N-cocodimethylamine oxide, N-lauryl dimethylamine oxide, N-myristyl dimethylamine oxide, N-stearyl dimethylamine oxide, N-cocamidopropyl dimethylamine oxide, N-tallowamidopropyl dimethylamine oxide, bis(2-hydroxyethyl) C12-15 alkoxypyrrolamine oxide.

[0024] Preferably a foam booster is selected from the group consisting of lauric acid diethanolamide, N-lauryl dimethylamine oxide, coconut acid diethanolamide, myristic acid diethanolamide, and oleic acid diethanolamide. The foam boosting agent is preferably present in the shampoo compositions of this invention in an amount from about 1 to 15 wt% and more preferably about 2 to 10 wt% based on the total weight of the composition.

[0025] A pH adjusting agent, preferably to adjust the pH within the range of 4 to 9 and more preferably within the range of 5 to 6 may also be used in the shampoo compositions of this invention. Any water soluble acid such as a carboxylic acid or a mineral acid is suitable. For example, suitable acids include mineral acids such as hydrochloric acid, sulfuric acid, and phosphoric acid, monocarboxylic acid such as acetic acid and lactic acid, and polycarboxylic acids such as succinic acid, adipic acid, and citric acid. The pH adjusting agent when used, is present in the shampoo compositions of this invention in an amount sufficient to provide a pH in the final shampoo composition of from 4 to 9, more preferably from 5 to 6. Preferably the pH adjusting agent is present in an amount from about 0.01 to 3 wt% and preferably about 0.1 to 0.5 wt% based on the total weight of the composition.

[0026] A thickening agent is preferably present in sufficient quantities to provide a convenient viscosity. For example, viscosities within the range of 500 to 25,000 mm<sup>2</sup>/s at 25°C or more preferably in the range of 3,000 to 7,000 mm<sup>2</sup>/s are usually suitable. Suitable thickening agents are exemplified by sodium alginate, gum arabic, polyoxyethylene, guar gum, hydroxypropyl guar gum, ethoxylated alcohols, such as laureth-4 or polyethylene glycol 400, cellulose derivatives exemplified by methylcellulose, methylhydroxypropylcellulose, hydroxypropylcellulose, polypropylhydroxyethylcellulose, starch, and starch derivatives exemplified by hydroxyethylamylose and starch amylose, locust bean gum, electrolytes exemplified by sodium chloride and ammonium chloride, and saccharides such as fructose and glucose, and derivatives of saccharides such as PEG-120 methyl glucose diolate or mixtures of 2 or more of these. Preferably the thickening agent is selected from the group consisting of cellulose derivatives, saccharide derivatives, and electrolytes, or from a combination of two or more of the above thickening agents exemplified by a combination of a cellulose derivative and any electrolyte, and a starch derivative and any electrolyte.

[0027] The thickening agent, where used is present in the shampoo compositions of this invention in an amount sufficient to provide a viscosity in the final shampoo composition of from 500 to 25,000 mm<sup>2</sup>/s. Preferably the thickening agent is present in an amount from about 0.05 to 10 wt% and preferably about 0.05 to 5 wt% based on the total weight of the composition.

[0028] Other optional components may be added to the shampoo compositions of this invention such as fragrances, preservatives, vitamins, ceramides, amino-acid derivatives, liposomes, polyols, such as glycerine and propylene glycol and botanicals (plant extracts) and additional conditioning agents such as quaternary polymers or silicone materials. The  
5 additional optional ingredients can be present up in an amount of up to 5 parts by weight per 100 parts by weight of optically clear shampoo composition, but preferably are present in amount of from 0.1 to 1 part by weight per 100 parts by weight of the shampoo composition.

10 [0029] The shampoo compositions of this invention may be in the form of a gel, paste, foam or a freely pourable liquid. The shampoo compositions of this invention can be used on the hair of humans or animals to cleanse and improve the appearance of their coats, respectively. The shampoo compositions of this invention are expected to be used by the usual method of adding the shampoo to the hair, massaging the shampoo into the hair and  
15 removing the shampoo from the hair by rinsing with water. The shampoo compositions may be prepared by simply mixing all ingredients together, and stirring them thoroughly. Heat may be applied to improve the dispersion of the ingredients.

[0030] Shampoo compositions according to the present invention provide superior  
20 conditioning benefits, including wet and dry hair detangling, a smooth hair feel and less yellowing, compared with other shampoos using traditional amino functional siloxane ingredients.

[0031] In another aspect the invention provides a leave-on conditioner which  
25 comprises an amine, polyol functional siloxane. Leave-on conditioners are known in the art, and have been described for example in patent specifications WO200108643, EP0945124, WO9962467 and WO09962468.

[0032] In yet another aspect the invention provides a hair colorant or hair dyeing  
30 composition which comprises an amine, polyol functional siloxane. These hair dyeing compositions may be oxidation or non-oxidation compositions, also sometimes referred to as permanent and semi-permanent oxidation compositions.

[0033] Oxidation hair dyeing agents are most widely used as permanent hair dyeing agents. Oxidation dye precursors in such hair dyeing agents penetrate into hair, and chemically impart a colour to the hair by means of colour formation resulting from oxidative polymerisation under the action of an oxidation agent. The process is generally one characterised by permanency in the dyeing effect. Non-oxidation dyeing agents are used for semi-permanent or non-permanent hair dyeing. Semi-permanent or non-oxidation dyeing agents are sometimes also referred to as direct dyes. Semi-permanent dyeing will usually colour human hair for up to six subsequent shampoo washes, although a high proportion of colour is often lost after 2 or 3 washes.

[0034] Semi-permanent hair dyeing compositions are usually provided as single-component products, and may contain a variety of additives in addition to a direct dye. As far as the forms of oxidation hair dyeing agents are concerned, numerous two-component type products are known. They are used by mixing, at the time of hair dyeing, a first agent containing an oxidation dye precursor, and a second agent containing an oxidation agent. There are also single-component products which are powder-like. These products are used by mixing the one component with water at the time of hair dyeing. Multi-component products containing three or more agents are also known.

[0035] With regard to oxidation hair dyeing agent compositions, a two-component type composition is particularly provided, and it contains as a first agent or component a mixture of an oxidation dye precursor, a cyclic silicone, an amino, polyol siloxane material, optionally an emulsifying agent, and water. This mixture is preferably emulsified in water using the emulsifying agent. The second agent or component of the composition is an aqueous hydrogen peroxide solution.

[0036] The hair dyeing agent compositions of the invention may also contain cyclic silicone materials, preferably in small proportions. These, generally volatile, materials are known in the cosmetic industry under The Cosmetic, Toiletry, and Fragrance Association (CTFA) name CYCLOMETHICONE. Reference may be had to the CTFA's International Cosmetic Ingredient Dictionary. Some representative examples are

octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, and  
dodecamethylcyclohexasiloxane. These cyclic polydimethylsiloxanes generally have a degree  
of polymerisation of 3 to 7. In addition, it is also possible to use cyclic  
polymethylhydrogensiloxanes, cyclic polymethylvinylsiloxanes, and cyclic  
5 polymethylphenylsiloxanes, with low degree of polymerisation. Such other cyclic silicones  
are also known in the cosmetic and silicone industry.

[0037] If desired, the cyclic silicone can be included as a separate component, or in a  
mixture with the amino, polyol siloxane material. Its content in a mixture with the silicone  
0 elastomer is preferably at least about 87 percent by weight, but its content may vary above or  
below this amount depending on the type and properties of the particular cyclic silicone used,  
as well as on the type and properties of the amino, polyol siloxane material. The cyclic  
silicone should, however, be readily miscible with other oily like ingredients included in the  
oxidation hair dyeing agent, and it should be easily emulsifiable in water under influence of  
15 an emulsifying agent. Thus, the mixture should exhibit a paste-like or soft gel-like  
consistency.

[0038] Although cyclic siloxanes are an optional ingredient, they are preferably used  
in a small amount where a paste-like or soft-gel like consistency is required. Where such  
20 consistency is required, too small an amount of the cyclic silicone in the mixture will not  
exhibit a paste-like or soft gel-like consistency. This may affect the amount of silicone  
elastomer available to adhere to the hair, with the result that it will have an effect on the  
ability to impart gloss and smoothness. For such applications the amount of cyclic silicone  
present preferably varies from 15-95 percent by weight, the remainder being the amino,  
25 polyol siloxane material.

[0039] The content of cyclic silicone and amino, polyol siloxane material in hair  
dyeing agent compositions of the invention is most preferably about 1.25 percent by weight,  
based on the total weight of the hair dyeing agent composition. If the amount is too large,  
30 then emulsification in water is difficult. If the content is too small, it is difficult to obtain any  
meaningful hair treatment effect. However, for most purposes, it has been found that the  
content can vary between 0.1-10 percent by weight. In addition, because the combination of

cyclic silicone and amino, polyol siloxane material is oil-soluble, the combination is preferably emulsified in water using an emulsifying agent.

[0040] The non-oxidation hair dyeing agent composition comprises a direct dye, which has been described for example in GB patent specification 2,173,515 and comprises anthraquinone, azo, nitro, basic, triarylmethane or disperse dyes or combinations thereof. Further disclosures of suitable dyes includes the article in Journal of the Society of Cosmetic Chemistry, 35, 297 to 310, of September/October 1984, entitled chemistry of hair colorant processes by John F. Corbett. It lists as suitable direct dyes nitrophenylene-diamine and nitroaminophenol derivatives, supplemented by some aminoanthraquinones. Examples include N-(2-hydroxyethyl)-2-nitroaniline, N-tris(hydroxymethyl)methyl-4-nitro-o-phenylenediamine, N-(2-hydroxyethyl)-2-nitro-p-phenylenediamine, N,N,N-tris(2-hydroxyethyl)-2-nitro-p-phenylenediamine, O,N-bis(2-hydroxyethyl)-2-amino-5-nitrophenol, 4-hydroxy-2'-nitrodiphenylamine, 4-amino-4'-bis(2-hydroxyethyl)-aminoazobenzene, 1,4,5,8-tetraaminoanthraquinone and 1,4-diaminoanthraquinone.

[0041] The amount of direct dye used in compositions according to the invention may range from 0,01 to 10% by weight of the composition. Suitably the dye, or when a mixture of dyes is used, each dye, may be present in an amount from 0.01 to 5% by weight, preferably 0.01 to 3% by weight, most preferably 0.1 to 1% by weight.

[0042] The oxidation hair dyeing agent component of the composition of this invention is an oxidation dye precursor, and it can be an indole or indoline such as are described in Japanese Kokai Patent Application Publication No. 08[1996]-040857/US 5690697 (November 1997). In addition, some examples of other types of oxidation dye precursors useful in the present invention include compounds such as *p*-phenylenediamine, *p*-nitro-*o*-phenylenediamine, *p*-chlor-*o*-phenylenediamine, *p*-nitro-*m*-phenylenediamine sulfate, and other phenylenediamines; toluene-2,5-diamine, toluene-3,4-diamine, toluene-2,5-diamine sulfate, 2,4-diaminophenoxyethanol chloride, and other diamines; *p*-aminophenol, *p*-methylaminophenol, *m*-aminophenol-*o*-aminophenol, 5-(2-hydroxyethylamino)-2-methylphenol and other aminophenols; aminonitrophenol, 4,4'-diaminophenylamine, and other diphenylamines; diaminophenylamines, N-phenyl-*p*-phenylenediamine, and other N-

phenylphenylenediamines; 2,6-diaminopyridine, 2,5-diaminopyridine, and other diaminopyridines; *p*-amino-*o*-cresol and other aminocresols; resorcinol; pyrogallol; phloroglucinol; catechol; and salts thereof.

5 [0043] While there are no particular limitations on the amount of oxidation dye precursor used, it should be present in amounts typically used in such applications, i.e., generally 0.05-10 percent by weight based on the weight of the hair dyeing agent composition.

10 [0044] The oxidation hair dyeing agent composition of the invention can be in a single-component form or a multi-component form made up of two or more agents. As a two-component form, for example, a suitable composition would include a two-part composition used by mixing at the time of hair dyeing, a first agent containing the oxidation dye, cyclic silicone, and silicone elastomer, with a second agent containing an oxidation  
15 agent. Alternatively, it could be in the form of a two-part composition used by mixing at the time hair dyeing, a first agent containing an oxidation dye, with a second agent containing the silicones and an oxidation agent. The ratio used for mixing together the first agent with the second agent should be 1:1, but other ratios can be employed, provided they do not result in any adverse effects such as sagging, usability, or evenness of dyeing.

20 [0045] Any conventional oxidation agent can be used for the oxidation hair dyeing agent composition according to this invention. Some examples of suitable oxidation agents are set forth in Japanese Kokai Patent Application Publication No. Hei 08[1996]-040851, referred to above. Thus, some representative and useful compositions include hydrogen  
25 peroxide, persulfuric acid salts, perboric acid salts, bromic acid salts, periodic acid salts, urea peroxide, percarbonic acid salts, peroxytripolyphosphoric acid salts, peroxybiphosphoric acid salts, and peroxyorthophosphoric acid salts. The most preferred oxidation agent based on its ease of use and general availability is a hydrogen peroxide solution.

30 [0046] Other ingredients can be included in the hair dyeing agent compositions of the invention provided the effects of the invention are not compromised. Some examples may be found in Japanese Kokai Patent Application Publication No. Hei 08[1996]-040851, referred



to above. Representative ingredient include materials, which in an oxidation hair dyeing agent composition are compatible with the first agent, but which are also useful in non-oxidation hair dyeing agent compositions, such as glycerin, propylene glycol, dipropylene glycol, polyethylene glycol, hyaluronic acid salts, diglycerin, 1,2-butylene glycol, pyrrolidone carboxylic acid salts, sorbitol, lactose, oligosaccharides, lanolin, squalane, liquid paraffin, Vaseline, higher fatty acids, triglycerides, and ester oils.

[0047] Additional examples of other ingredients are thioglycolic acid salts, L-ascorbic acid salts, hydrogen sulfites, hydrosulfites, hydrogen sulfates, and other anti-oxidants and stabilizers; collagen hydrolyzate, gelatin hydrolyzate, silk protein hydrolyzate, elastin hydrolyzate, soybean protein hydrolyzate, and other protein hydrolyzates and their quaternary derivatives; ammonia water, alkanolamine, ammonium carbonate, sodium hydrogen carbonate, potassium hydroxide, and other alkali agents.

[0048] Because combinations including cyclic silicones, silicone elastomers, and other oil-soluble ingredients, are not easily dissolved in water, it is preferred to emulsify these materials in water using an emulsifying agent. Some examples of suitable nonionic surface active agents are polyoxyethylene alkyl ethers, polyoxyethylene fatty acid esters, polyoxyethylene polyhydric alcohol fatty acid partial esters, polyoxyethylene hardened castor oil derivatives; octylpolyglycoside; polyglycerin fatty acid esters, polyglycerin alkyl ether; maltitol hydroxyalkyl ether, other sugar-alcohol hydroxyalkyl ethers; and fatty acid diethanolamide. Some anionic surface active agents which can be used include higher fatty acid salts, alkylbenzenesulfonic acid salts, phosphoric acid esters, alkylsulfuric acid salts, alkylsulfuric acid esters, and polyoxyethylene alkylsulfuric acid esters. Representative cationic surface active agents are amino acids, alkyltrimethylammonium salts, dialkyldimethylammonium salts, and alkyldimethylamine oxides. Mixtures of these surface active agents may also be employed.

[0049] Still further examples of other ingredients which can be included with the compositions are ethanol, butanol, propanol, isopropanol, benzyl alcohol, and other lower alcohols; 2-ethylhexyl alcohol, 2-hexyldecyl alcohol, 2-decyltetradecyl alcohol, isostearyl alcohol, cetostearyl alcohol, lauryl alcohol, stearyl alcohol, cetyl alcohol, and other higher

alcohols; hydroxyethane diphosphonic acid, phenacetin, EDTA, and salts thereof; parabens, stannates, and other sequestering agents and anti-septic agents; poly(dimethylallyl ammonium halide)-type cationic polymers, cationic polymers formed by condensation of tallowyl amine obtained from beef tallow fatty acids, propyleneamine, epichlorhydrin, and polyethylene glycol; cationic polymers formed by condensation of cocoyl amine obtained from coconut oil fatty acids, propyleneamine, epichlorhydrin, and polyethylene glycol; cationic polymers of dimethylamino methacrylate copolymer; cationic polymers of cellulose ether containing quaternary nitrogen; lauric acid diethanolamide, carboxymethyl cellulose, carboxyvinyl polymer, hydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, xanthan gum, carrageenan, alginic acid salts, pectin, furcellaran, gum arabic, tragacanth gum, agar, bentonite, cross-linkable polyacrylic acid salts, and other such thickeners; pH adjusting agents, fragrances, plant extracts, and drugs.

[0050] Some examples of ingredients suitable for combining with the second agent of oxidation hair dyeing agent compositions, or for use in non-oxidation hair dyeing agent compositions, include phenacetin, EDTA, and their salts; parabens, stannates, and other sequestering agents and anti-septic agents; liquid paraffin, Vaseline, and other oily ingredients; 2-ethylhexyl alcohol, 2-hexyldecyl alcohol, 2-decyltetradecyl alcohol, isostearyl alcohol, cetostearyl alcohol, lauryl alcohol, stearyl alcohol, cetyl alcohol, and other higher alcohols; polyoxyethylene alkyl ethers, alkylsulfuric acid ester salts, acylmethyl taurine, and other surface active agents; acids such as citric acid, malic acid, acetic acid, lactic acid, oxalic acid, tartaric acid, formic acid, levulinic acid, and other organic acids; phosphoric acid, hydrochloric acid, and other inorganic acids; pH-adjusting agents, fragrances, plant extracts, drugs, dyes, and water. If it is desired to include the cyclic silicone and silicone elastomer in the second agent instead of, or in addition to the first agent, the silicones should be emulsified in water using an emulsifying agent.

[0051] For semi-permanent dyeing, the composition is applied to the hair, left for a time, according to the extent of dyeing required, and rinsed off with water. For oxidation compositions, the dyeing process is carried out by applying the oxidation hair dyeing agent composition of the invention to hair, and after allowing the oxidation hair dyeing agent composition to penetrate into the hair, it should remain on the hair for 5 to 30 minutes,

preferably about 10 to 20 minutes, at normal temperature in the range of 15-40 °C. The hair should then be washed with shampoo or soap containing water, and rinsed with water to wash away any remaining oxidation hair dyeing agent composition.

5 [0052] The compositions according to the invention showed an improved retention of colour upon exposure to ultraviolet light, in comparison with hair which was coloured with compositions not comprising the amino, polyol functional siloxane material. There is also an improvement in colour intensity.

10 [0053] Different aspects of the invention is illustrated by the following Examples, in which all parts and percentages are by weight, and viscosities are measured at 25°C and atmospheric pressure.

Example 1.

15 [0054] A silanol end-blocked with a viscosity of approximately 60 cP (71 parts), aminoethyl-aminoisobutyl methyl dimethoxy silane (5.7 parts) and a C<sub>13</sub>-C<sub>15</sub> aliphatic alcohol (19 parts) were charged to a three necked flask fitted with a condenser and thermometer, upon which they were heated to 85°C, at which time 0.07 parts of barium  
20 hydroxide and 0.03 parts of tri-sodium orthophosphate were added, and the mixture kept at 85°C for a further two hours under nitrogen. The reaction mixture was then devolatilised at 85°C under reduced pressure (100 mbar) for four hours. The mixture was allowed to cool to 30°C, and it was filtered to remove any solid catalyst. The resulting hazy fluid was an amino-functional polydimethylsiloxane copolymer end capped with a mixture of C<sub>13</sub>-C<sub>15</sub> alkoxy,  
25 methoxy and silanol end groups. The reaction mixture was then cooled to 50°C upon which glycidol (8.0g) was added. The reaction was held at 50°C for four hours and then heated to 85°C and held at this temperature for a further two hours. The resulting clear fluid was an aminopolyol-functional polydimethylsiloxane copolymer end capped with C<sub>13</sub>-C<sub>15</sub> alkoxy,  
30 methoxy and silanol end groups. The polymer had a viscosity of 4,000 mm<sup>2</sup>/s, with a nitrogen content of about 0.7%. The amino substituents on the siloxane backbone had the

following structure:  $\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{N}(\text{Z})\text{CH}_2\text{CH}_2\text{NZ}_2$ , wherein Z denotes a group –  $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ .

[0055] The following tests are being carried out on hair in the application examples  
5 below: wet combing evaluation, dry combing evaluation, hair gloss evaluation, shine and colour evaluation on grey hair static and fly-away of hair.

[0056] Wet combing evaluation is being done by using ready prepared slightly  
bleached swatches or oriental hair of 2 g, 25 cm and a Matador® comb, reference 2618/6 –  
10 GB. The swatches are pre-treated by washing, using 5 g of the 30% sodium lauryl sulphate (SLS) solution (Empicol LX28/Albright & Wilson), stroking the tresses downward and leaving the surfactant to act for 30 sec, followed by rinsing the swatches for 1 minute with tap water at 37°C, removing the excess of water, allowing the swatches to dry overnight on a paper towel (Room Temperature). The swatches are then treated with solvent to standardise  
15 them and remove traces of SLS: and allowed to dry overnight on a paper tissue (Room Temperature). Every new hair batch must undergo, after the washing and pre-treatment, a validation in order to set a baseline for the combability. Three sets of tresses are combed by each of the panellists. After treatment with the shampoo or leave-on conditioner, each panellist takes the top of the tress to be tested in the palm of the hand, holding it with the  
20 fingers and combs the tress along the volar forearm of the other hand. The time to detangle a tress is measured in seconds and entered in a table.

[0057] Dry combing evaluation is carried out by running sensory evaluation using a triangular test, which is a known test in sensory evaluation.

[0058] Hair gloss evaluation. The test consists of comparing treated pairs of swatches in a shine box according to their level of gloss. Following statistical evaluation of the opinions of the panellists conclusions are drawn.

30 [0059] Static and fly away of hair is designed to measure the ability of various products and formulations to affect the relative static reaction of hair. It is assessed by

measuring and comparing the opening angle of hair tresses after dry combing at constant humidity and temperature against a rectangle panel of 45 cm of width and 31 cm of height with drawn increasing angles is realised. A first measurement of the angle is made before combing by aligning the tress on the central line ( $\angle_{\text{bef}}$ ) and a second measurement of angle is made after having passed the comb 3 times through the swatch ( $\angle_{\text{aft}}$ ). This is repeated for 5 swatches per product application. The difference is calculated: ( $\angle_{\text{aft}}$ ) - ( $\angle_{\text{bef}}$ ). A statistical t-test is conducted on the 5 values (differences) per product, in order to show significant differences of static behaviour between the different tested products.

## 10 Example 2

[0060] A clear shampoo composition was prepared, using the polymer of Example 1 comprising Empicol ESB 3 (30parts), Amonyl 380BA (4 parts), Crothix 2602 (2 parts), polymer JR 400 (0.1 parts) water (10 parts), Rewomid IPP 240 (2 parts), Polymer of Example 1 (2 parts), additional water (up too 100 parts of the composition in total), and small quantities of NaCl to stabilise the composition. Hair swatches are treated by wetting 5 tresses of hair for 30 sec with tap water at 37°C, followed by lathering the 5 tresses for 30 sec. with 4g of shampoo (0.4g of shampoo per 1g of hair), stroking the tresses downward and letting them stand to act for 30 sec. Then the 5 tresses are rinsed for 1 minute with tap water at 37 °C, the excess of water is removed by stroking the tresses three times between 2 fingers. Lay them down on a paper towel ready for testing or drying at room temperature. Example shampoo using amino, polyol functional siloxane of Example 1 (ES), was compared with a control C (no use of shampoo, but merely wetting in water), with a commercial shampoo CS, not containing a silicone product, and with a amino siloxane, not having polyol functionality (AS). The wet combing evaluation gave the following results (in seconds):

ES: 12.84 C: 27.60 CS: 20/79 AS: 19.81

Fly away was tested and found to be least for ES. A sensory evaluation was done by a panel, in comparison of ES with C, and the following were found (1 is excellent, 5 is poor):

	ES	C
Ease of dry combing	2.6	3.5
Fly away when dried	2.4	2.4
Feel when dried	2.7	3.5
Body and volume	2.6	3.0
Shine	2.4	3.6
Fly away during drying	2.0	2.5
Ease of setting	3.0	2.9
Ease of combing during drying	3.0	3.2
Ease of wet detangling	3.2	3.4
Wet feel of rinsed hair	2.8	3.1
Ease of rinse	2.9	2.3
Foam feel	2.6	2.9
Foam elasticity	2.5	3.3
Foam quantity	2.4	3.1

Yellowing was also studied in a spectrophotometer, and found to be very similar to Control, and substantially improved over AS.

### 5 Example 3

[0061] A first leave on conditioner formulation was prepared by mixing 1.5 parts of Brij 30 and 20 parts of Brij 35 (as a 20% solution), followed by adding 20 parts of the amino, polyol siloxane of Example 1, and mixing this till homogeneous. The mixture was then  
 10 heated to 65°C, and, while mixing, slowly 58,5 parts of water were mixed until homogeneous. The mixture was then allowed to cool to room temperature while continuing the mixing.

[0062] A second, clear water based, leave-on conditioner was prepared by mixing  
 15 Arquad 16-29W (0.3%), Example 1 amino, polyol siloxane in microemulsion form (5%), D-Panthenol (0.2%), Propylene Glycol (0.5%) and Phenonip (0.1%), adjusting the pH to 4 with

citric acid 50% solution, heating 10% of the water (sufficient needed to add up to a total of 100% in the formulation) to 60°C, and mixing until dispersed. The mixture was then allowed to cool down to room temperature, and the remaining water was added, with a renewed adjustment of the pH to 4 with citric acid 50% solution

5

[0063] A third clear leave on conditioning agent was prepared by mixing 2 parts of Example 1 amino, polyol siloxane material with 98 parts of a 50/50 mixture of octamethyl cyclotetrasiloxane and decamethyl cyclopentasiloxane, with some traces of Parsol MCX.

10

[0064] Hair swatches were treated by dipping 1 tress at a time 3 times in 37°C tap water and removing excess of water by stroking the tress between 2 fingers. The tress was laid down on a clean support and all along the tress a quantity of product was applied using a calibrated micropipette. The product used was emulsified and diluted to 6% active material, using 100 microliter (0.1g) per tress. The tress was then submitted to panellist to carry out tests as described above. Tresses were allowed to dry overnight. The treated samples were tested for wet detangling, comparing samples EC (example conditioner, results were equivalent for first, second and third composition described above), C (control, merely using water), CC (commercial conditioner, not using any siloxane) and ASC (using prior art amino siloxane, not having polyol functionality). Results in seconds were as follows:

15

20 EC: 8.59 C: 20.24 CC: 13.54 ASC 8.36

The samples were also tested for shine, and showed an improved hair shine when the example conditioner was used.

## Example 4

[0065] A semi-permanent dyeing composition was prepared comprising:

ED		PAD	CD
Base O/W 097	28%	28%	28%
Propylene glycol	4%	4%	4%
Phenoxetol	0.30%	0.30%	0.30%
Solvariane	9%	9%	9%
Covariane Rouge W3123	2.00%	2.00%	2.00%
Covastyle TBQ	0.20%	0.20%	0.20%
Silicone	1.4%	1.4%	0.0%
Disodium EDTA	0.25%	0.25%	0.25%
2-amino-2-methyl-1- propanol at 10%	to pH 6	to pH 6	to pH 6
Water	to 100%	to 100%	to 100%

5

[0066] This was prepared by the following method comprising using a mixing vessel, to melt the Base O/W at 70°C while stirring, while in another container, weighing out the Solvariane, Phenoxetol, Propylene Glycol, Covariane and Covastyle, dissolving them completely with stirring and heat gently at 40-50°C, then adding this solution to the base O/W 097, rinsing the container with a part of hot water, and then adding the rest of hot water, followed by stirring until the mixture is homogenous, and adding the disodium EDTA, allowing the mixture to cool to room temperature, before adjusting the pH to 6 with AMP and compensating for the water loss. This composition was then applied to hair by wetting 5 tresses under running water at 37°C, during 30sec, followed by lathering them with 5 ml colouring cream, applied uniformly, for 1 minute and packing the tresses in aluminium foil and letting them rest for 30 minutes, after which the 5 tresses were wetted each with 1 ml water and lathered for 30 sec, and then rinsed under running water at 37°C, during 4 min (until the water is clear). The tresses were then hung to dry at room temperature.

15



[0067] The treated tresses were compared for colour intensity, showing that the Control Dye (CD) and the prior art Dye (PAD) gave a reading on grey hair in the colorimeter of 37 for L\*, whereas the example formulation (ED) gave a value of 34, showing a much improved intensity of colour. Upon exposure to UV light over several weeks, the following results were obtained in percentage based on colour intensity at the start:

Formulation	After 0 weeks	After 1 week	After 2 weeks	After 3 weeks	After 4 weeks
CD	100%	102%	103%	98%	95.5%
PAD	100%	102%	93%	90.5%	89.5%
ED	100%	105%	104%	100.5%	99.5%

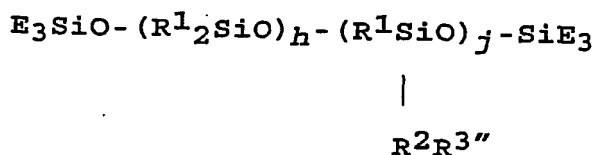
[0068] A permanent dyeing composition was prepared. The treated tresses were compared for colour intensity, as it was followed over a period of 2 weeks, showing that the Control Permanent Dye (CPD) gave a reading for L\* on grey hair in the colorimeter of 36.75 at start and 35.7 after 2 weeks, Prior Art Permanent Dye (PAPD) gave a reading for L\* on grey hair in the colorimeter of 36.55 at start and 36.25 after 2 weeks, whereas the example formulation (EPD) gave a value of 35.2 at start and of 34.95 after 2 weeks, showing a much improved intensity of colour. Upon exposure to shampooing, the following results were obtained in percentage based on colour intensity at the start:

Formulation	After 0 shampoos	After 5 shampoos	After 10 shampoos
CPD	100%	97.6%	94.0%
PAPD	100%	98.6%	96.0%
EPD	100%	99.6%	99.5%

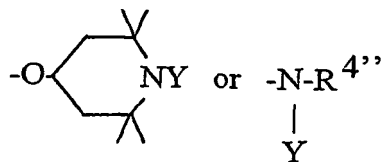
## CLAIMS

1. A hair care composition comprising an amino, polyol functional siloxane material.
2. A hair care composition according to Claim 1, wherein the amino, polyol functional siloxane material is the reaction product of an organopolysiloxane having at least one unit of the general formula  $\text{O}_{3-a/2}\text{SiX}_a\text{-R-NH-R'}$  and at least one unit of the general formula  $\text{O}_{4-b/2}\text{Si-X}_b$  with one or more monoepoxides wherein X denotes a monovalent hydrocarbon group having up to 8 carbon atoms, R denotes a divalent alkylene group, R' denotes a hydrogen atom or a group of the formula RZ wherein Z is NHX,  $\text{NH}_2$ ,  $\text{NHRNH}_2$  or  $\text{NHRNHX}$ , *a* has a value of 1 or 2 and *b* has a value of 2 or 3.

3. A hair care composition according to Claim 1 or 2, wherein the amino, polyol functional siloxane material has an average general formula



wherein each E is independently selected from a monovalent hydrocarbon group, a hydroxyl group or an alkoxy group; each R<sup>1</sup> is independently a monovalent hydrocarbon group; each R<sup>2</sup> is independently a divalent hydrocarbon group having 1 to 10 carbon atoms; *h* is 25 to 1,000; *j* is 0.1 to 200; and each R<sup>3</sup> is a heterocyclic nitrogen-containing group



wherein each R<sup>4''</sup> is independently selected from a hydrogen atom or a group of formula -R<sup>2</sup>NY<sub>2</sub>, each Y is independently a hydrogen atom or Y', and each

Y' is a group of formula  $-\text{CH}_2(\text{OH})-\text{CHR}^2-\text{OH}$ , wherein  $\text{R}^2$ , which can be the same or different, is characterized as above, and with the proviso that every Y is not H.

4. A hair care composition according to any preceding claim, wherein the amino, polyol functional siloxane material is prepared by reacting an amino functional siloxane with a monoepoxide which is an epoxy functional alcohol compound having a general formula:



where  $\text{R}^2$  is a divalent hydrocarbon group.

5. A hair care composition according to Claim 4, wherein the epoxy functional alcohol is glycidol, 2,3-epoxy-cyclopentanol or 3,3-epoxy-6-methylcyclohexylmethanol.
6. A hair care composition according to anyone of the preceding claims, which also comprises one or more additional ingredients selected from surfactants, thickeners, rheology modifying additives, perfumes, waxes, emollients, cleaning agents, lubricating oils, electrolytes, flavouring agents, biocides, pharmaceutical or cosmetic active materials.
7. A hair care composition according to anyone of the preceding claims, which also comprises a polysiloxane polyoxyalkylene copolymers.
8. A hair care composition according to anyone of the preceding claims, which is selected from a shampoo composition, a leave-on conditioners, a semi-permanent colorants or a permanent colorant composition.
9. A hair care composition according to anyone of claims 1 to 8, which is a

shampoo composition comprising an amino, polyol functional siloxane, and at least one anionic deterative surfactant, and optionally a foam boosting agent, a pH adjusting agent, a thickening agent, and water.

10. A hair care composition according to anyone of claims 1 to 8, which is a leave-on conditioner which comprises an amine, polyol functional siloxane,
11. A hair care composition according to anyone of claims 1 to 8, which is a hair dyeing composition.
12. A hair care composition according to anyone of the preceding claims, which also comprises a volatile siloxane compound.

## INTERNATIONAL SEARCH REPORT

Internat. Classification No.  
PCT/EP 03/01076A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

28 May 2003

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# INTERNATIONAL SEARCH REPORT

Intern: Application No  
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